

Ammonia plasma passivation of GaAs in downstream microwave and radio-frequency parallel plate plasma reactors

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The poor electronic properties of the GaAs surface and GaAs-insulator interfaces, generally resulting from large density of surface/interface states, have limited GaAs device technology. Room-temperature ammonia plasma (dry) passivation of GaAs surfaces, which reduces the surface state density, is investigated as an alternative to wet passivation techniques. Plasma passivation is more compatible with clustered-dry processing which provides better control of the processing environment, and thus, improves interface integrity. Passivation was monitored in real-time and *in situ* using photoluminescence (PL). In addition, the passivated surfaces are inspected using x-ray photoelectron spectroscopy. Passivation with two different plasma excitation methods, downstream microwave (2.45 GHz) and rf (13.56 MHz) parallel plate, are compared, and effects of operating parameters such as pressure, flow rate, and power are examined. In both methods plasma-generated H atoms reduce the surface state density by removing excess As and As₂O₃ during the first few seconds of the plasma exposure. This step is followed by formation of Ga₂O₃ which takes place on a longer time scale (5–10 min). While the final passivation result appears to be similar for both methods, surface damage by ion bombardment competes with passivation in the parallel plate method, reduces the PL yield and adversely affects the long term stability of the passivated surface. Although it is common to heat the sample during passivation, we show that NH₃ plasma passivation is possible at room temperature without heating. Low-temperature processing is important since passivation can be done at the end of device processing when it is undesirable to expose the device to elevated temperatures. The absence of ion bombardment damage combined with efficient generation of H atoms in the downstream microwave treatment, make this scheme a preferred dry passivation process, which could be easily and inexpensively clustered with existing GaAs processes.

I. INTRODUCTION

The poor electrical properties of the GaAs surface and GaAs-insulator interfaces, generally resulting from large density of surface/interface states, have limited GaAs device technology. Unlike silicon, whose oxide passivates the silicon surface leaving a low density of interface states, the native oxide of GaAs does not so passivate the GaAs surface. In fact, the interface between GaAs and its native oxide, a mixture of arsenic oxides and gallium oxides, can be laden with defects which create a large interface state density in the midband gap.^{1–5} This results in a high recombination velocity and Fermi level pinning which in turn affect the performance of devices such as field effect (FET) and heterojunction bipolar transistors (HBT).^{1–30} Increased leakage currents in FETs and photodiodes, and emitter size effect in HBTs are among the problems caused by undesired interface states.^{6–8}

Passivation of GaAs surfaces by wet or dry processes has received well-deserved attention and a number of processes have been shown effective in reducing the GaAs

surface state density.^{8–30} Successful liquid passivation schemes were developed by Sandroff *et al.* using Na₂S–9H₂O,^{9,10} Yablonovitch *et al.*,¹¹ Fan *et al.*,^{12,13} and Shikata *et al.*⁸ used inorganic sulfides such as (NH₄)₂S to treat the GaAs surface. Surface treatments using Na₂Se, As₂Se₃ diluted in NH₄OH solutions and other solutions containing S, Se, or ammonia were also shown to be effective in passivating GaAs.^{14–19}

Plasma passivation is more compatible with the current integrated circuit manufacturing technology which increasingly favors clustered, dry processing. Clustered-dry processing provides better control of the processing environment, reduces sources of contamination, and thus, improves the interface integrity. Therefore, it is desirable to develop dry-passivation methods to replace the wet-passivation techniques. It has been shown that exposure of the GaAs surface to H₂ plasmas results in the reduction of surface states.^{8,20–29} In some of the plasma passivation processes, H₂/N₂,^{8,22,23} NH₃,^{8,20,30–33} or H₂S³⁴ discharges were also used. Nitrogen-containing plasmas were proposed to form a thin layer of high band gap GaN on the GaAs surface.⁵ To this end, Theeten *et al.*²² and Friedel and Landesman²³ used N₂ multipolar plasmas at elevated temperatures (>200 °C) to form GaN. Callegari *et al.*²⁴ used rf N₂ plasma to form GaN. In these treatments, N₂ plasma exposure followed a H₂ plasma treatment. Clearly, NH₃ plasmas allow the sample to be exposed to both N and H

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atoms simultaneously. In addition to H_2 and N_2 , Pankove *et al.*²⁰ used a rf NH_3 plasma to passivate GaAs, and investigated the effect of surface temperatures ranging from 100 to 500 °C. Pankove found that high temperature was necessary for the formation of GaN which was believed to have passivated the surface. Cassette *et al.*,³⁰ Proust *et al.*,³² and Wu and Lin³¹ all used rf NH_3 plasmas at elevated temperatures (150–350 °C) to passivate GaAs prior to silicon nitride or silicon oxynitride depositions. Similarly, Li *et al.*³³ used electron cyclotron resonance H_2 , N_2 , and NH_3 plasmas to treat GaAs at 250 °C.

In all of the above studies, some form of surface quality and/or device performance improvements were reported. Although the detailed mechanism of plasma passivation is not well-understood, there is evidence in the literature that atomic hydrogen is largely responsible for the improvement in surface quality by removing the As antisite defects and arsenic oxides.^{5,8,20–33} However, it is not clear if the formation of GaN further improves the surface quality or what the effect of plasma parameters are on the quality of passivation.

There are a large number of process parameters such as the plasma excitation method, power, pressure, flow rate and composition of gases, sample temperature, and treatment time. With a few exceptions,^{28,31} most passivation studies to date have not concentrated on the optimization of these parameters. This is partly due to lack of *in situ* diagnostic methods to monitor the passivation process. The success of the passivation method was generally evaluated, after processing, by performance of the devices. In fact, Gottscho *et al.*, using *in situ* photoluminescence (PL) measurements, showed that the conditions commonly used in rf parallel-plate reactors for H_2 plasma passivation were far from optimal.²⁸

The objective of this study is to investigate the NH_3 plasma passivation process to understand phenomena occurring during NH_3 plasma passivation and to optimize process parameters. We report results of room-temperature (25 °C) NH_3 passivation of GaAs using a remote (downstream) microwave and a rf parallel-plate plasma reactor. Passivation of GaAs is monitored real-time and *in situ* using PL.²⁸ PL provides the means to monitor changes in the surface recombination velocity, and the kinetics of passivation as a function of the process parameters. In general, PL yield increases as interface states are eliminated and surface recombination velocity is decreased.^{35–37} Thus, higher PL yield implies better surface quality and a better passivated surface. In addition to *in situ* PL monitoring, the passivated surfaces are inspected using x-ray photoelectron spectroscopy (XPS). Auger electron spectroscopy (AES), and secondary ion mass spectrometry (SIMS).

In this study, passivation with two different plasma excitation methods, downstream microwave and rf parallel plate, are compared and effects of operating parameters such as pressure, flow rate, and power are examined. While the surface reactions and passivation mechanism seem to be similar for both methods, surface damage by ion bombardment competes with passivation in a parallel-plate plasma reactor and reduces the PL yield by introducing

new surface states. The ion bombardment damage also degrades the long term stability of the passivation. The damage mechanism is absent in the downstream microwave plasma since the discharge is isolated from the sample. As previously reported, pressure and exposure time are the critical parameters in a rf plasma passivation.²⁸ In microwave downstream passivation, choice of power, pressure, and flow rate determine the passivation rate, and hence, the plasma exposure time required. Downstream plasma passivation is faster at lower pressures (0.5–1 Torr), high microwave input power, and high flow rates. Although it is common to heat the sample during passivation,^{30–34} we show that NH_3 passivation is possible at room temperature without heating. This is important, since it allows passivation to be done at the end of device processing when it is undesirable to expose the device to elevated temperatures. Finally, phenomena occurring on the surface during passivation are discussed, in light of PL and XPS data.

II. EXPERIMENT

The experimental system and procedures used in this study have been described previously.^{28,38,39} The reactor, consisting of a six-way Pyrex cross and two parallel-plate electrodes, has since been modified to include a quartz inlet tube where a microwave plasma could be sustained. Thus, the reactor could be used as a rf (13.56 MHz) parallel-plate or a microwave (2.45 GHz) downstream reactor. In the parallel-plate mode of operation, the plasma is sustained between two equal area 7.6 cm diam electrodes separated by 3 cm. rf power is applied to the upper anodized Al electrode through a matching network, and the GaAs sample is placed on the lower, stainless-steel electrode which is grounded. In the downstream mode, the plasma is excited in a 2.54 cm diam quartz tube enclosed in a 5 cm long microwave (2.45 GHz) cavity. The quartz tube has a bend immediately after the microwave cavity to reduce the amount of radiation the sample receives. Radicals produced in the plasma travel ~14 cm before reaching the six-way Pyrex cross. The gas flow expands into the Pyrex chamber and the radicals travel approximately another 14 cm before reaching the sample which is placed on the lower electrode. A schematic of the experimental apparatus is shown in Fig. 1.

The *in situ* PL diagnostic arrangement (Fig. 1) is similar to that of Gottscho *et al.*²⁸ Briefly, a pulsed (20 Hz) N_2 pumped dye laser beam (600 $\mu J/cm^2$ at 500 nm) (Moletron) passes through a fiber and is focused onto the samples placed on the grounded electrode. PL is collected perpendicular to the laser propagation direction, imaged onto a fiber bundle after passing through a spectral filter, and detected using a photomultiplier tube (PMT). The output of the PMT is monitored using a gated integrator (SRS Model 250) interfaced with an AT&T personal computer. Depending on the time resolution needed to resolve PL intensity changes, 5–40 laser shots are averaged.

Samples used are rectangular pieces (~1.5 cm \times 0.8 cm) of semi-insulating GaAs. As previously,²⁸ samples are dipped in HF for 30 s, washed with de-ionized water, blow dried with N_2 and loaded into the reactor. The reactor base

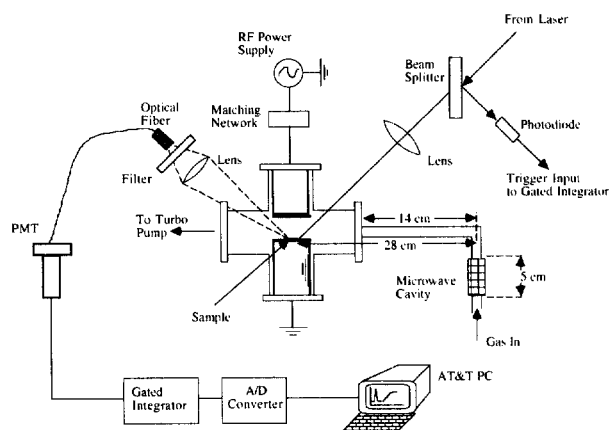
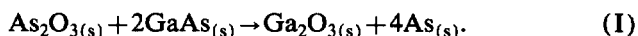


FIG. 1. Schematic of the experimental system.

pressure, after 24 h of pumping, is 1.7×10^{-7} Torr. However, experiments are started after sample loading and ~ 1 h of pumping. At this time, the reactor base pressure is less than 10^{-6} Torr. While the reactor is open for sample loading, the chamber is purged with dry nitrogen to minimize moisture contamination.

III. DOWNSTREAM MICROWAVE PASSIVATION

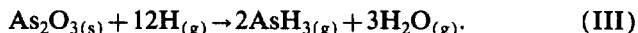
There is mounting evidence in the literature that As antisite defects are responsible for pinning the Fermi level and increasing the surface recombination velocity.¹⁻⁵ Excess As is formed by the solid-state reaction of the native oxide layer with the underlying GaAs,⁵



Exposure of the GaAs native oxide layer to H atoms has been shown to result in removal of As, and As_2O_3 from the surface, via the presumed reactions,



and



Removal of both As and As_2O_3 from the surface reduces the As antisite defects, and thus, decreases the surface recombination velocity which further results in enhanced PL yield.

Figure 2(a) shows the PL intensity as a function of time for a GaAs sample during treatment with a downstream microwave NH_3 plasma. Plasma operating conditions are 1 Torr, 140 W, and 10 sccm NH_3 . Concentrating on Fig. 2(a), one observes two processes, with distinct time scales. The PL intensity increases drastically by a factor of 10 immediately after the plasma is gated on at $t=1$ min. Following this sudden jump, the PL intensity reaches a short-lived plateau [indicated as I in Fig. 2(a), and hereafter, referred to as the first plateau] and slowly increases again, reaching a second plateau marked as II on Fig. 2(a). After the plasma is turned-off, the PL intensity increases abruptly to reach its final value ~ 20 –25 times the initial (unpassivated) PL level [marked as III on Fig. 2(a)].

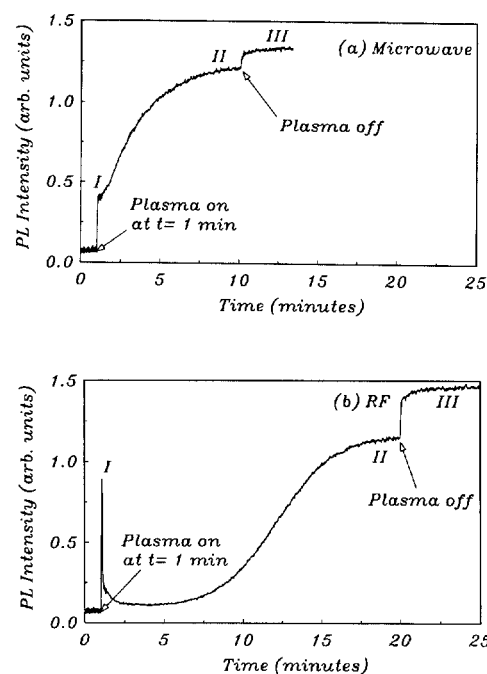


FIG. 2. GaAs PL intensity as a function of time for (a) 1 Torr, 140 W downstream microwave plasma and (b) 4 Torr, 20 W, rf parallel-plate plasma. Ammonia flow rate was 10 sccm and sample temperature was 25 °C for both experiments.

Hydrogen atoms are created in the plasma via electron impact dissociation of NH_3 and are transported via convection and diffusion to the GaAs surface. We surmise that H atoms chemisorb onto the GaAs surface and react with As and As_2O_3 , to form AsH_3 . The removal of As and As_2O_3 reduces arsenic antisite defects leading to an immediate increase in PL intensity. This initial PL increase during NH_3 plasma passivation is similar to the behavior of PL intensity in H_2 plasma which supports the conclusion that H radicals play the central role in increasing PL.²⁸ Examination of the passivated surfaces using XPS corroborates the hypothesis that the As_2O_3 is removed during the initial stages of passivation. Figures 3(a)–3(c) show the

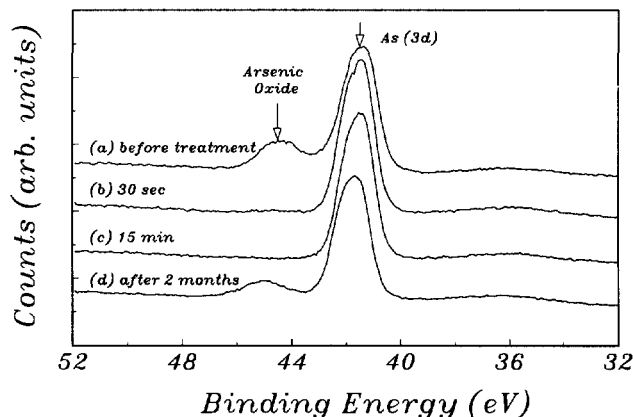


FIG. 3. As(3d) XPS spectrum (a) prior to plasma treatment, (b) after microwave plasma treatment for 30 s, (c) after treatment for 15 min. Spectrum (d) is that of a passivated sample after two months.

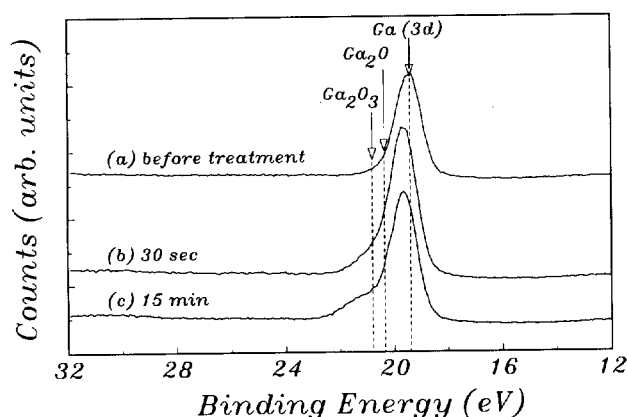


FIG. 4. Same as Fig. 3 except Ga (3d) peak.

As (3d) XPS peaks for three samples. Spectrum (a) corresponds to that of a standard sample which has been HF dipped for 30 s (but not plasma passivated), while spectra (b) and (c) correspond to samples that have been NH_3 plasma passivated for 30 s and 15 min, respectively. The oxide component, shifted 2.9 eV from the As (3d) bulk peak, has completely disappeared after 30 s of plasma treatment. Thus, the process with short time scale is the removal of arsenic oxides, and is completed within a few seconds of exposure of the sample to the plasma effluent, downstream from the discharge.

Exposure of the sample to air, after passivation, can alter the surface and the XPS results which warrants discussion. In a previous study, sample transfers to the XPS chamber in an Ar glove bag instead of air exposure gave the same results.²⁸ The absence of As_2O_3 from the XPS spectra taken *ex situ*, after the sample has been exposed to air, indicate that As_2O_3 forms on a much longer time scale than the time it took us (typically 5 min) to transfer the sample to the XPS chamber. Our recent, *in situ* attenuated total reflection-Fourier-transform infrared (ATR-FTIR) spectroscopy studies of the surface is consistent with the XPS results, and we believe that the air exposure does not alter the surface appreciably in the time it takes us to transfer the samples to the XPS chamber.

Comparison of the Ga (3d) XPS peaks for samples exposed to plasma effluent for different durations indicate that the PL increase from the first plateau to the second plateau is due to plasma assisted modification of the gallium oxide which remains after removal of the arsenic oxides. Figure 4 shows the Ga (3d) XPS peaks for three samples. As in Fig. 3, spectrum (a) corresponds to that of a standard sample which has been HF dipped for 30 s (but not plasma passivated), while spectra (b) and (c) correspond to samples which have been passivated for 30 s and 15 min, respectively. Clearly, the oxidized component of Ga (3d) increases as the GaAs surface is exposed longer to the downstream microwave NH_3 plasma. Deconvolution of the bulk Ga (3d) peak and the oxidized component in spectra (b) and (c) reveals that the oxidized component is shifted with respect to the bulk contribution by 1.0 eV for the sample exposed to plasma for 30 s and by 1.4 eV for

sample exposed for 15 min. Gourrier *et al.*⁴⁰ isolated two different oxide contributions on the GaAs surface by examining high resolution spectra measured with synchrotron radiation. One of the two components was shifted by 1.4 eV with respect to the bulk contributions while the other was closer to the bulk peak, shifted by 0.9 eV. Gourrier *et al.*⁴⁰ ascribed these two peaks to Ga_2O_3 and Ga_2O , respectively. Thus, the XPS data suggest that the time from the first PL plateau to the second PL plateau in Fig. 2(a) corresponds to formation of gallium oxide and transformation from Ga_2O to Ga_2O_3 .

Although the formation of GaN has been proposed and observed after NH_3 plasma treatments at high temperatures, no evidence of GaN was present on the samples analyzed by XPS. Auger analysis of a treated sample showed less than 3% N on the surface. Formation of GaN seems to require high temperature (200–600 °C) and an ultrahigh vacuum environment in order to thermally desorb or reduce the gallium oxide. Unlike arsenic oxides, gallium oxide is not easily removed by reaction with H atoms and may form easily in presence of oxygen atom sources such as water vapor. In this study, the sample was at room temperature making reduction of the gallium oxide and formation of GaN unlikely. Even if the gallium oxide could be reduced, the base pressure of our system (10^{-7} Torr) is not low enough to keep the oxide from reforming.

The sudden increase in the PL intensity upon gating the plasma off [Fig. 2(a)] was observed previously during rf diode plasma passivation.²⁸ This “jump” was suggested to be due to the charging (discharging) of the surface when the plasma is turned-on (-off).²⁸ However, charging is unlikely in the microwave downstream plasma treatments where the plasma is 28 cm away from the sample. In addition, no current could be detected at the lower electrode in the presence of the plasma, indicating that ions do not reach the substrate. The sudden increase is observed for both H_2 and NH_3 plasma treatments in both the microwave downstream and rf diode reactors. We attribute this sudden increase to rapid desorption of H atoms from the surface when the plasma and thus the production of H atoms is turned-off. The dynamic equilibrium between the surface and the H containing gas over the sample is disturbed when the plasma is gated-off. Reversible and irreversible changes in the PL intensity with adsorption of gases such as H_2O , O_2 , BCl_3 , and Cl_2 on GaAs has been reported in the literature.^{39,41} Similar to such effects, H adsorption on the surface could introduce surface states and decrease PL intensity. In fact, consistent with this hypothesis, Bartels *et al.*⁴² found that H atom adsorption on GaAs (110) creates adsorption-induced surface states at 0.85 and 0.63 eV above the valence band.

A. Effect of plasma exposure time

Investigating the effect of sample exposure to the plasma provides more insight into the changes that the surface undergoes during passivation. Figure 5 shows the effect of exposure time on the PL intensity at 2 Torr, 140 W microwave power with 10 sccm NH_3 flow rate. The plasma

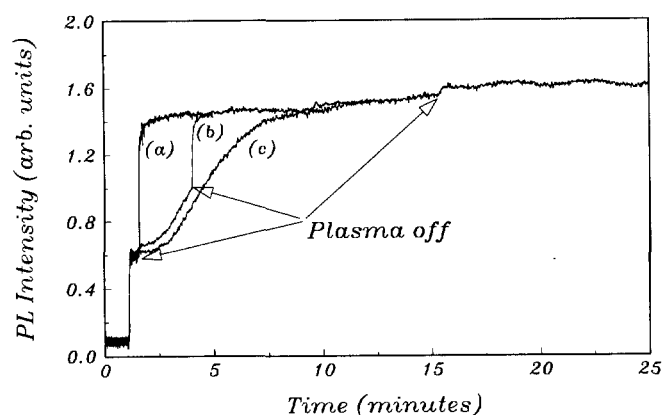


FIG. 5. The effect of exposure time on the PL intensity for (a) 0.5, (b) 3, and (c) 14 min at 2 Torr, 140 W microwave power with 10 sccm NH_3 flow rate.

was turned-on at $t=1$ min and turned-off after 0.5, 3, and 14 min for curves (a), (b), and (c), respectively. Irrespective of when the plasma is turned-off, the PL intensity jumps approximately to the same final value. The magnitude of the jump is smaller for longer exposure times. One sample which was treated over 1 h (not shown on Fig. 5) showed no jump in the PL intensity when the plasma was turned-off. Instead, the PL intensity asymptotically approached the final PL level of about 1.5 arbitrary units. Although the final PL intensity is nearly the same for all three plasma exposure times, the surfaces at the end of each treatment are expected to be different. First, as shown in the XPS spectrum of Fig. 4, the samples exposed for shorter times have less and perhaps a different type of gallium oxide on the surface than those exposed for longer times. Second, samples exposed for shorter times, are less stable, especially in ambient air, than those exposed for longer times (see Sec. III C).

Another difference between the shorter exposed (30 s) and the longer exposed (15 min) samples is depicted in Fig. 6. Figure 6 shows the PL intensity as a function of time for two samples treated under the same conditions as in Fig. 5. The plasma is turned-off after 30 s (on the first plateau) in both cases and turned back on after 2.5 [curve (a)] and 20 min [curve (b)], respectively. During the time that the plasma is off, the NH_3 flow is maintained. The PL instantly increases to the second plateau upon turning off the plasma. When the plasma is turned-on again, the PL level decreases to the same level as the first plateau and passivation continues as if the plasma were never turned-off. In contrast to these results, when a sample passivated for longer than 15 min [e.g., the sample in Fig. 5, curve (c)] is reexposed to the NH_3 plasma the PL level does not change.

On the first plateau, the surface should be hydrogenated. We surmise that the increase in PL is stopped from reaching the final intensity (≈ 1.5 arbitrary units), corresponding to "complete" passivation, because adsorbed H atoms create new surface states, and thus, additional non-radiative recombination centers.⁴² These adsorbed H atoms

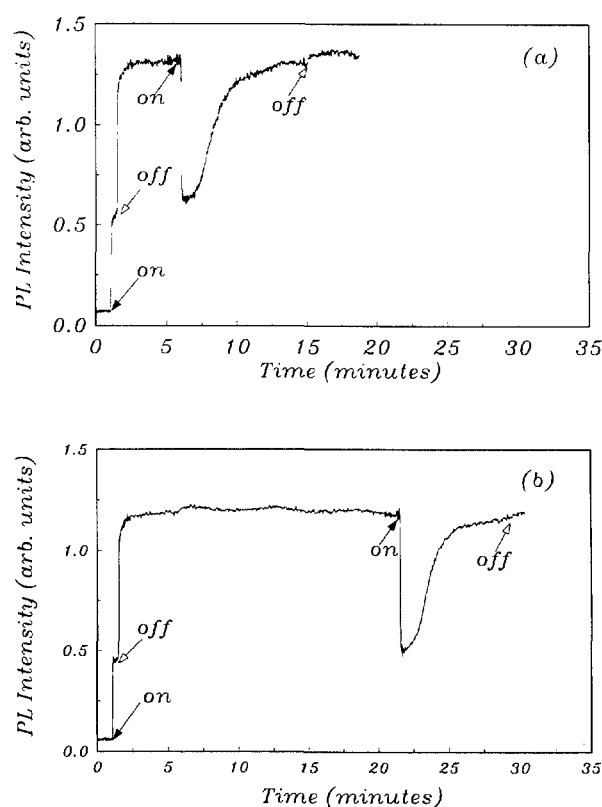


FIG. 6. PL intensity as a function of time for microwave plasma treatments at 2 Torr, 140 W, and 10 sccm NH_3 flow rate. Plasma was turned-on/off at indicated times.

are in dynamic equilibrium with the surface. Molecular hydrogen forms on the surface via H atom recombination and desorbs while H atoms formed in the plasma adsorb on to the surface. Competing with this adsorption/desorption process is oxidation of the GaAs surface. While As_2O_3 is removed as it forms by reaction with H, Ga_2O_3 remains. Both residual H_2O present in the plasma and oxygen from the reduced As_2O_3 can act as sources for oxygen atoms. Preliminary *in situ* ATR-FTIR spectroscopy of the surface during passivation indicates that the source of oxygen is physisorbed H_2O on the GaAs surface produced by reaction of H atoms with As_2O_3 . ATR-FTIR data also show that the H atoms react with the quartz tube to form water which is transported downstream to the sample where it physisorbs on the surface. (Results of ATR-FTIR measurements will be presented in a future publication.) As the gallium oxide covers the surface and thickens, the PL intensity increases. The formation of the oxide layer may alter the way in which H atoms are adsorbed onto the surface, thereby diminishing their effect on the GaAs-oxide interface, where recombination processes take place.

Results of the experiments shown in Fig. 6 confirm that the surface is modified during the slow rise from the first plateau to the second plateau. The abrupt increase and decrease when the plasma is turned-off and -on is attributed to H atoms desorbing and adsorbing from the surface. During the slow rise, as the surface is modified and gallium oxide forms on the surface, it becomes increasingly difficult

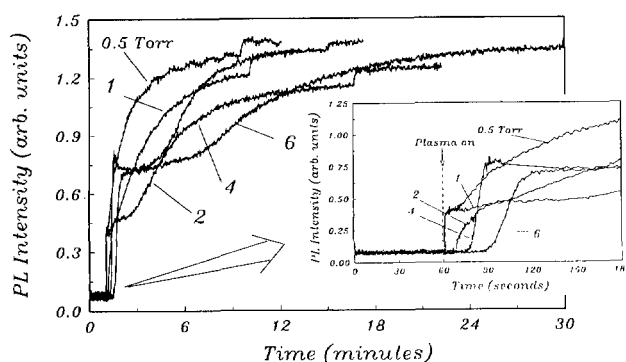


FIG. 7. PL intensity as a function of time for different process pressures. The time scale is expanded in the inset to show the initiation period (see text).

for H to induce traps at the oxide-substrate interface and PL intensity increases. At the end of a 15 min or longer passivation, gallium oxide covers and passivates the GaAs surface. Interestingly, the presence of plasma (i.e., H atoms) is needed for the reactions leading to the formation of gallium oxide during the slow rise from the first plateau to the second plateau. These results show that H atom plays an essential role in the gallium oxide formation. A possible overall reaction for this step is



The standard-free energy change for this reaction is -582 kcal/mol. In the solid state, this reaction could proceed via oxygen surface diffusion, H adsorption, and possibly transformation of the gallium oxide surface (consistent with the XPS data). We note that this proposed overall reaction (IV) is subtly different than the reactions (II) and (III) which are generally presumed to be the reactions responsible for the removal of surface As and As_2O_3 . Unlike reaction III, water is not a produce of reaction IV. We surmise that the oxygen in the native oxide layer does not leave the surface during the passivation process [e.g., as water, as in reaction (III)] and simply redistribute over the surface according to reaction (IV) to transform As_2O_3 to Ga_2O_3 . Recently, Mikhailov *et al.*⁴³ during XPS investigation of interaction between H and native oxide of GaAs, also found that the reduction of arsenic oxide at low substrate temperatures (150°C) is accompanied by formation of gallium oxide according to reaction (IV).

B. Effect of pressure, power, and flow rate

Pressure, microwave power, and gas flow rate influence the passivation process through their effect on H concentration in the reactor and transport of H atoms to the sample surface. Figure 7 shows the PL intensity as a function of time for several different pressures as GaAs samples are treated with a downstream microwave NH_3 plasma operating at 140 W and 10 sccm. After the microwave plasma is ignited, there is an initiation period (see the inset in Fig. 7) during which the H atom concentration in the plasma increases and H atoms are transported downstream

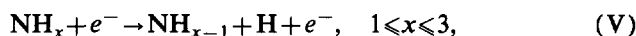
to the sample. This initiation time is shorter for high gas flow rates and low pressures since the average velocity of the gas,

$$u = \frac{Q}{A} = \frac{Q_0 P_0 T}{A P T_0}, \quad (1)$$

is proportional to the flow rate in sccm, Q_0 (subscript 0 denotes STP conditions) and inversely proportional to the gas pressure, P . In Eq. (1), T is the temperature of the gas, and A is the cross-sectional area of the tube. Assuming that the convective transport dominates over the diffusive transport in the axial direction, the time for the H atoms to reach the sample, after turning on the plasma, is simply the length of the tube leading to the sample divided by the average velocity in the tube. Using the dimensions of our system, we calculate initiation times 10, 20, and 30 s at 2, 4, and 6 Torr, respectively, in reasonable agreement with Fig. 7. At lower pressures (≤ 1 Torr), diffusive transport becomes important, and we do not expect this simple calculation to be accurate.

After the H atoms reach the sample, reactions (II) and (III) take place rapidly, eliminating a nonradiative recombination pathway, and leading to an abrupt increase in PL intensity. The PL intensity reaches the first plateau (see for example, curves in Fig. 7 for 1–6 Torr, the plateau at 0.5 Torr is less evident and lasts ~ 10 s) as these reactions reach completion. Both the first plateau and the overall passivation takes longer at higher pressures presumably, because of lower H concentration over the surface. Hydrogen atom concentration can decrease with increasing pressure because of higher recombination rate in the gas and lower convective and diffusive transport rates as discussed below.

The decrease in H concentration with increasing pressure can be understood by considering the production and loss mechanisms of H atoms in the NH_3 plasma. Hydrogen atoms are produced by electron impact in the plasma via reactions,



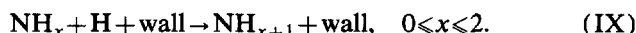
and consumed by volume recombination reactions,



and



where M is a third body. Hydrogen also recombines on the reactor walls via the heterogeneous recombination reactions,



All reactions (V)–(VIII) take place in the section of the tube enclosed by the microwave cavity, where the plasma is sustained, but only the reactions (VI)–(IX) take place in the section downstream from the plasma. The rates of the reactions leading to loss of H (VI)–(IX) all increase with increasing pressure. In particular, the rate of the three body gas phase recombination reactions (VI) and (VII)

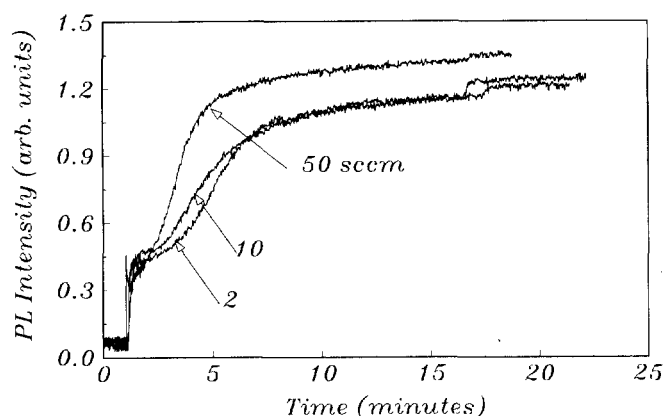


FIG. 8. PL intensity as a function of time for different NH_3 flow rates.

increase at least linearly with pressure since the concentration of the third bodies increase. The pressure dependence of H atom production can be complex. Using FTIR absorption, we measured that the partial pressure of the NH_3 above the sample (downstream from the plasma) is 10%–20% of the total pressure when the microwave power is greater than ≈ 100 W. This result is approximately independent of the pressure and indicates that at least 80% of the NH_3 is dissociated in the plasma. Since almost all of the NH_3 is dissociated, we expect the H concentration in the plasma to increase at most linearly with pressure. In addition, both axial convection and diffusion transport slow down with increasing pressure (i.e., greater residence time at higher pressures). Hydrogen atoms have more time to interact with the tube walls and recombine before they can reach the sample. At higher pressures, fewer H atoms are brought to the sample, placed downstream from the plasma, and thus, the passivation process takes longer time.

Figure 8 shows the effect of NH_3 flow rate on passivation. Other process conditions were 2 Torr and 140 W. Passivation is faster at higher flow rates, because the flux of H atoms to the GaAs surface is higher. More H atoms are brought to the sample by convection before they recombine on the tube walls or in the gas phase.

Figure 9 shows the effect of power on passivation. At lower microwave input power, the electron density is lower and fewer NH_3 molecules are dissociated to form H. This result is confirmed by FTIR absorption measurements, which indicated that the fraction of NH_3 dissociated ($\{P_T - P_{\text{NH}_3}\}/P_T$, where P_T is the total pressure and P_{NH_3} is the partial pressure of NH_3) increases linearly from 25 to ≈ 75 W and begins to saturate at $\approx 85\%$, when the microwave power is greater than ≈ 100 W. Thus, at low microwave powers, as a result of the reduced H production rate, both the H concentration in the plasma and the H flux to the GaAs surface are reduced, which slows the passivation process. For example at 25 W, even after 19 min of plasma treatment, passivation is incomplete and a large PL jump is observed, when the plasma is turned-off at $t=20$ min. In contrast to the 25 W experiment, at 140 W passivation is complete after ≈ 10 min. While the difference in time to

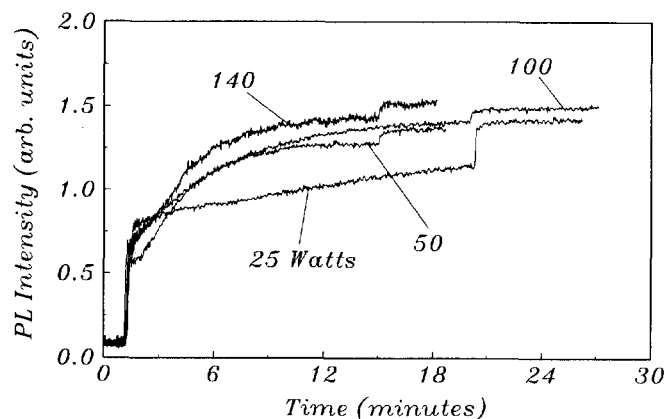


FIG. 9. PL intensity as a function of time for different microwave input powers.

complete the passivation is obvious between the 25 and 50 W experiments, this difference is less obvious between the 100 and 140 W passivation. This is because of the saturation of fraction of NH_3 dissociated with microwave power. Since almost all the NH_3 is dissociated, further increase in power above ≈ 100 W does not increase the H production rate appreciably.

C. Stability of passivation

An important consideration in passivation is the stability of the passivated surface. Passivated surfaces need to be stable upon exposure to the ambient air at least long enough for the processing steps to be completed and/or the device to be capped. Figures 10(a) and 10(b) show the long-term stability of the PL intensity for samples treated with a microwave plasma for 9 min or longer. The solid lines are exponential fits to the data drawn to aid the eye. The data in Fig. 10(a) are for samples kept in a dry box purged with nitrogen while the data in Fig. 10(b) are for samples kept in ambient air without any special precaution. Samples kept in the dry box lose only $\sim 40\%$ of their PL intensity over a month. The final intensity is still ten times greater than the PL intensity for unpassivated GaAs. The PL intensity of the samples kept in the ambient air decay faster (half-life, $\tau_{1/2}=14$ days) than the samples kept in dry box ($\tau_{1/2}>35$ days). This suggests that O_2 and/or water vapor in the ambient air contribute to the decay in PL intensity. As (3d) XPS spectrum of a sample which is stored in ambient air for two months subsequent to passivation is shown in Fig. 3, curve (d). The arsenic oxide component which was eliminated by plasma treatment has grown back and is likely to be responsible for the reduced PL intensity. This was also observed with H_2 rf plasma treatments previously.²⁸ The oxygen atoms from adsorbed water vapor and/or O_2 can diffuse through the gallium oxide to the GaAs interface and react with GaAs to form As_2O_3 which can further react according to reaction (I) to form As antisite defects. The stability behavior of samples treated with a plasma for less than 30 s confirm this hypothesis. Figure 11 shows the PL intensity data for three samples. Two of these samples were treated for 30 s

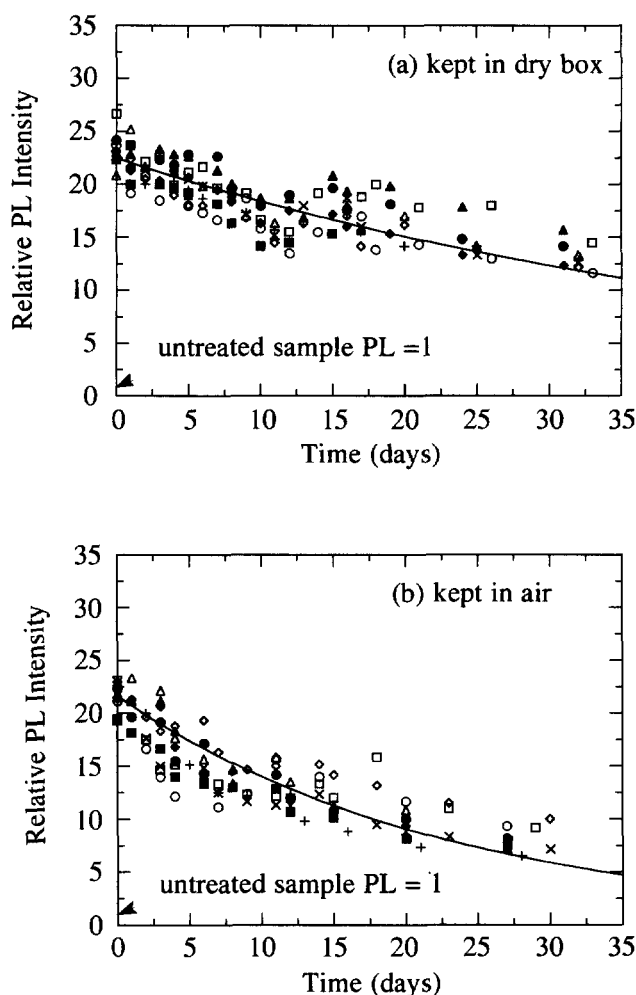


FIG. 10. PL intensity data for several samples, microwave plasma passivated for over 9 min and (a) kept in dry box or (b) in ambient air. Relative PL intensity is defined as the PL intensity divided by the unpassivated PL value.

while a third was treated for 10 s. Other plasma treatment conditions were identical for all three samples at the base conditions. One of the 30 s treated samples was kept in dry box while the other samples were kept in air. As shown in Fig. 11, the PL intensity of all three samples decay dramatically over a period of few days, much faster than the samples treated completely for 9 min or longer. The passivation of these samples are stopped before a sufficiently thick gallium oxide layer is formed (see Fig. 4). Thus, the oxygen atoms can diffuse easily through the thin oxide and react with underlying GaAs to form arsenic oxides. The difference in stability of the samples which are kept in a dry box and in air is even more apparent in Fig. 11.

IV. rf PARALLEL PLATE PLASMA PASSIVATION

Figure 2(b) shows the PL intensity as a function of time as the GaAs samples are treated with a parallel-plate rf NH_3 plasma. The plasma is sustained at 4 Torr, with 20 W power, and 10 sccm NH_3 flow rate. The behavior of the PL intensity versus time is similar to Fig. 2(a), PL intensity

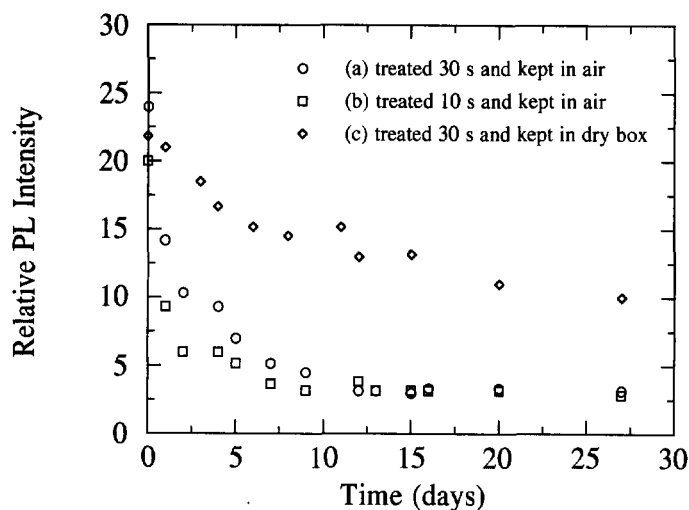


FIG. 11. GaAs PL intensity data for samples which are microwave plasma treated for <30 s. Sample (a) was treated for 30 s and kept in air. Sample (b) was treated for 10 s and kept in air. Sample (c) was treated for 30 s and kept in a dry box.

for a microwave treatment. Again, as in the microwave passivation, the PL intensity as a function of time reveals two processes with different time scales. However, instead of reaching the first plateau as in the microwave treatment, the PL intensity decreases rapidly after the first few seconds of direct exposure and abrupt increase to point I. After a few minutes, PL intensity starts to gradually increase again until it reaches a plateau in 20 min [indicated as II on Fig. 2(b)]. Finally, as in the microwave treatment, the PL intensity increases suddenly to the final PL level (III) when the plasma is switched-off.

In the parallel-plate reactor, the plasma is directly over the sample surface which is bombarded and damaged by energetic ions. This surface damage is presumably responsible for the immediate decrease of the PL after the first few seconds of passivation and has been observed previously in H_2 plasmas under conditions which promote energetic ion bombardment.²⁸ In this respect, NH_3 plasma passivation is similar to H_2 passivation in a parallel-plate reactor. The damage occurs faster in NH_3 plasma than H_2 plasma presumably because the surface is bombarded by heavier NH_3^+ ions ($0 < x < 3$) as compared to H_2^+ or H^+ ions. For example, the energy transfer efficiency, $E_T = 4M_1M_2/(M_1+M_2)^2$ is 5% for the H_2^+ impacting onto GaAs surface as compared to 38% for NH_3^+ . In the expression for E_T , M_1 and M_2 are the masses of the bombarding ion and the substrate molecule, respectively. Thus, the energy is transferred seven times more efficiently from NH_3^+ to the GaAs surface than from H_2^+ . In the NH_3 plasma, the peak-to-peak voltage measured was ~ 500 V and independent of pressure from 1 to 8 Torr. The time average sheath potential seen by the ions is ≈ 80 V.^{44,45} Assuming a typical $500 \mu\text{m}$ sheath thickness and $100 \mu\text{m}$ mean free path at 4 Torr, the average energy of the ions bombarding the surface would be ≈ 30 eV. Additionally, although most ions undergo collisions and lose energy, some ions can make it through the sheath without colli-

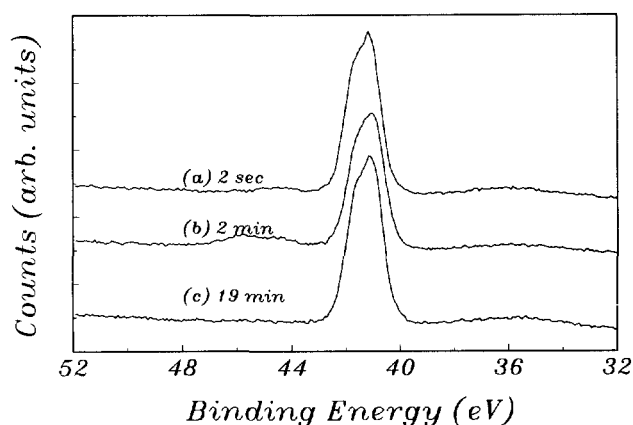


FIG. 12. As(3d) XPS spectrum after rf plasma treatment for (a) 2 s, (b) 2 min, and (c) 19 min.

sions and impact the surface with ≈ 80 eV. The magnitude of the ion energy is enough to break bonds and cause damage to the surface.

During the period between 1 and 20 min, it appears that a gallium oxide forms in lieu of the damaged surface. Indeed, XPS analysis of samples treated for 19, 2 min, and 2 s (Figs. 12 and 13) showed that the longer treated sample had more oxygen and Ga_2O_3 on the surface than the shorter treated samples. The 2 s and the 2 min treated samples also had detectable, but far less As_2O_3 than an untreated sample while the 19 min treated sample had no detectable As_2O_3 .

A. Effect of plasma exposure time

Figures 14(a)–14(c) show the PL intensity as a function of time for samples treated for 2 s [curve (a)], 6 s [curve (b)], and 2 min [curve (c)]. The process during the initial stages is unforgiving and even a few seconds delay in turning the plasma off drastically affects the final PL level attained. Ion damage occurs rapidly after the initial maximum in the PL. In fact, part of this decrease in PL could be due to H atoms adsorbing on to the GaAs surface as discussed in Sec. III A. For the samples exposed to the

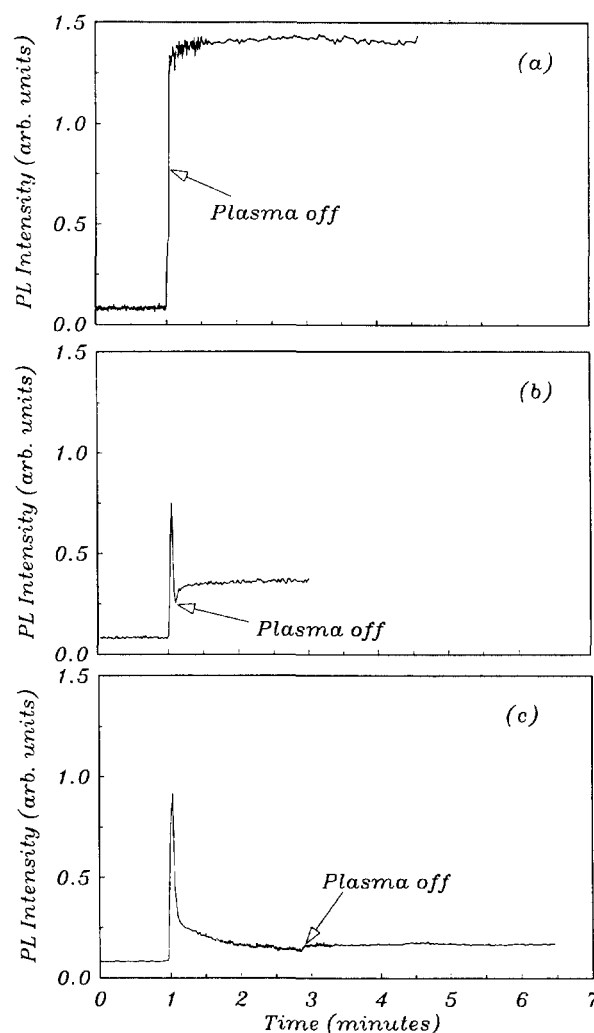


FIG. 14. The effect of exposure time on the PL intensity for (a) 2 s, (b) 6 s, and (c) 2 min at 4 Torr, 20 W rf power with 10 sccm NH_3 flow rate.

plasma longer than 2 s, the PL intensity increase suddenly to a higher level when the plasma is turned-off and H atoms desorb from the surface. However, because of surface damage, the final PL level attained is far below the PL for samples in Fig. 2 curve (b).

B. Effect of pressure, power, and flow rate

In rf parallel-plate passivation, power, pressure, and flow rate affect the process through their influence on the ion bombardment of the GaAs and reactor surfaces. In this respect, the most critical of the three variables are pressure and rf power. The flow rate did not have a significant effect on the rf parallel-plate passivation.

Figure 15 shows the PL intensity as a function of time for a low pressure [curve (a) 0.5 Torr] and a high power passivation [curve (b), 50 W]. At low pressure, the mean free path of the ions between inelastic collisions is larger. As a result, the ions can gain more energy from the sheath fields and strike the surface with higher energy than at high

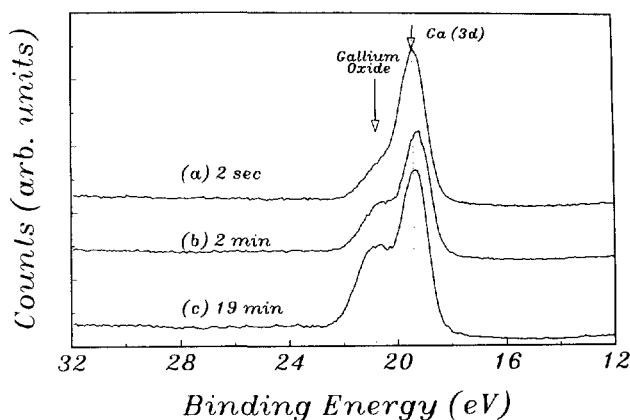


FIG. 13. Same as Fig. 12 except Ga(3d) peak.

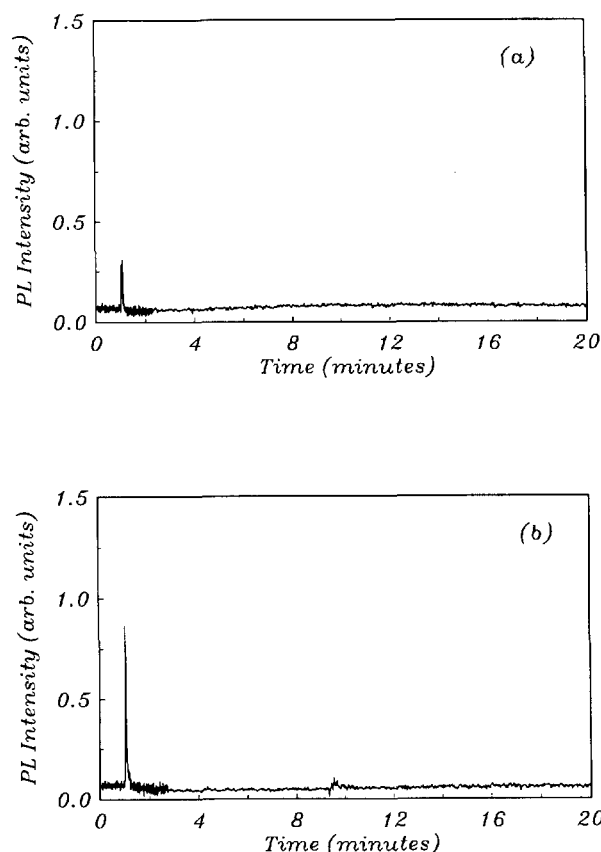


FIG. 15. PL intensity as a function of time for rf parallel-plate plasma treatment at (a) 0.5 Torr, 20 W and (b) 4 Torr, 50 W. Ammonia flow rate and treatment time were 10 sccm and 19 min for both experiments. Number of laser shots averaged was increased after the initial transient. This is the reason for decreased noise in the PL intensity after few minutes.

pressure. This damage at low pressure is irreversible and unlike the high pressure treatment [Fig. 2, curve (b)] the PL intensity does not increase.

The effect of power [Fig. 15(b)] is similar to that of pressure. Increasing the rf power also increases the peak-to-peak voltage, and thus, the sheath potential. Although the sheath thickness may also change with power, this change should be relatively small. As a result, the ions are accelerated through a higher sheath field and strike the sample and electrode surfaces with higher energy. High-energy ion bombardment damages the surface, introducing new surface states. The damage after the initial increase in PL is immediate and PL declines precipitously never recovering again.

After low-pressure and high-power experiments, we also found that our baseline experiment at 4 Torr, 20 W, and 10 sccm NH_3 flow rate could not be reproduced until the next day or until the reactor walls are "reconditioned" for 1 h or more. Ion bombardment of the electrode can contaminate the plasma and the GaAs surface or affect the H concentration in the reactor by changing the surface recombination rate. Passivation changes the surface subtly and it comes as no surprise that it is sensitive to such effects. In contrast, these effects are not observed in the

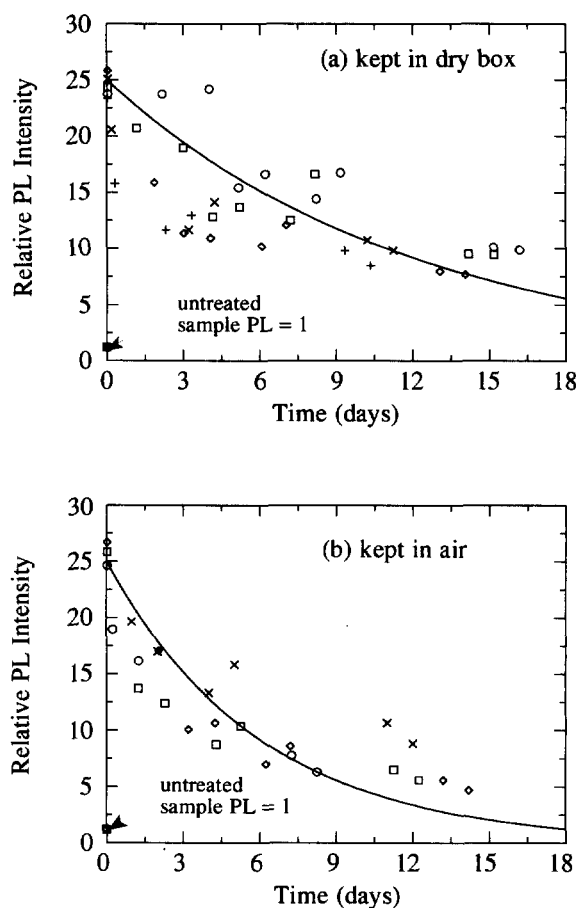


FIG. 16. Passivated GaAs PL intensity data for several samples, which are rf parallel-plate plasma passivated and (a) kept in dry box or (b) in ambient air. Relative PL intensity is defined as the PL intensity divided by the unpassivated PL value.

downstream microwave reactor, since the plasma is sustained without electrodes. This robustness is an advantage of the downstream plasma passivation as compared to rf parallel plate.

C. Stability of passivation

The rf plasma passivated samples are less stable than samples treated with downstream microwave plasma. The rf plasma passivated GaAs PL intensity data for several samples over a period of two weeks are shown in Figs. 16(a) and 16(b). All samples are treated either for 2 s or 19 min, with no apparent difference in stability between the two sets. In two weeks, the rf passivated samples, kept in a dry box, lost 70% of their PL intensity [Fig. 16(a)]. The PL decay of the samples kept in air is even worse [Fig. 16(b)]. The half-life, $\tau_{1/2}$, of the treated samples kept in ambient air and dry box were 4 and 8 days, respectively. The difference in decay times of the samples kept in air and samples kept in dry box indicate that the decay mechanism is similar to that of microwave plasma passivated samples, as discussed in Sec. III C. The faster decay of the rf plasma passivated samples can be attributed to a poorer quality of the gallium oxide formed on the surface as com-

pared to microwave treated samples. The gallium oxide formed under ion bombardment could have more voids and defects, and therefore, allow oxygen atoms from ambient air to diffuse to the GaAs interface more readily to form As_2O_3 .

V. SUMMARY AND CONCLUSIONS

Passivation with two different plasma excitation methods, downstream microwave (2.45 GHz) and rf (13.56 MHz) parallel plate, are compared and the effects of operating parameters such as pressure flow rate and power are examined. In both methods, H atoms, produced in the plasma, reduce the surface states by removing the As and As_2O_3 during the first few seconds of plasma exposure. Removal of As and As_2O_3 is followed by the formation of gallium oxide which takes place on a longer time scale (5–15 min). Hydrogen atoms produced in the plasma apparently participate in the formation of gallium oxide. While the final passivation results and surface reactions seem to be similar for both methods, surface damage by ion bombardment competes with passivation in the parallel-plate plasma reactor and reduces the PL yield by introducing new surface states. Ion bombardment damage also adversely affects the long term stability of the passivation. rf plasma passivated samples are less stable than the microwave downstream plasma passivated samples.

Although it is common to heat the sample during passivation, it is shown that NH_3 passivation is possible at room temperature without heating. Low temperature processing is important since passivation can then be done at the end of device processing when it is undesirable to expose the device to elevated temperatures.

In microwave downstream passivation, choice of power, pressure, and flow rate determine the passivation rate, and hence, the plasma exposure time required. Downstream plasma passivation is faster at lower pressures (0.5–1 Torr), high microwave input power and high flow rates presumably because of higher H atom flux to the surface. Ion bombardment damage is absent in the downstream microwave plasma. As a result, the quality of passivation is less sensitive to the exposure time and process variables than the rf plasma passivation. The improved stability of the microwave plasma passivated surface as compared to rf plasma passivated surface is attributed to absence of ion bombardment in the former method. In addition, microwave plasma excitation does not require electrodes which can be a source of surface contamination. Above advantages of the downstream microwave plasma passivation render it an inexpensive and efficient method that can easily be clustered with an existing process.

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